HALOGEN DERIVATIVES

OF

CERTAIN AZO DYES.

By

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Dept. of Chemistry.

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The object of this work is to compare the effects of Iodine, Bromine and Chlorine in the para position to the amino group of aniline, which has been diazotised and coupled with naphthalene 2-hydroxy 3-6-di-sulphonic acid and naphthalene 2-amino 8-hydroxy 6-sulphonic acid.

Experimental.

Para Iodo-aniline was prepared by treating aniline with iodine in the presence of calcium carbonate, water and ether. The proportions used were as follows;

22.4 gm. aniline
54 gm. iodine
25 gm. calcium carbonate
40 c.c.water
40 c.c.ether

This mixture was heated under a reflux condensor on a water bath for six hours. The para iodo-aniline was separated by steam distillation.

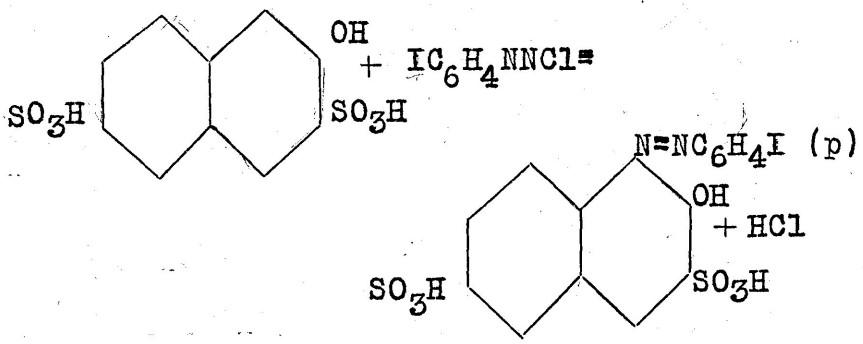
Para iodo-aniline coupled with naphthalene 2-hydroxy 3-6-di-sulphonic acid.

Equal molar parts of the following were used:

Naphthalene 2-hydroxy 3-6-di-sulphonic acid, para iodo-aniline and sodium nitrite. The para iodo-aniline was dissolved in hydrochloric acid and the temperature reduced to 3 C. The sodium nitrite was dissolved in hydrochloric acid and its temerature reduced to 3 C. The sodium nitrite solution was slowly added to the iodo-aniline, with constant stirring. This results in the formation of p-iodo-benzene diazonium chloride, according to the following equation:

$$IC_6H_4NH_2 + HNO_2 = 2H_2O + {}^{(p)}IC_6H_4NNCl$$

The naphthalene 2-hydroxy 3-6-di-sulphonic acid was dissolved in strong sodium hydroxide solution and cooled to 3 C. To this solution, the diazonium chloride was slowly added with constant stirring. This results in the formation of the dye, naphthalene 1-NNC_6H_4I 2-hydroxy 3-6-di-sodium sulphonate according to the following equation:



After the dye had been allowed to stand for a short time to insure the completion of the reaction it was salted out by the addition of common salt. The precipitated dye was filtered out and washed to free it as much as possible from sodium chloride. The dye was then analyzed for sodium, showing it to be naphthalene 1-NNC$_6$H$_4$I 2-hydroxy 3-6-di- sodium sulphonate.

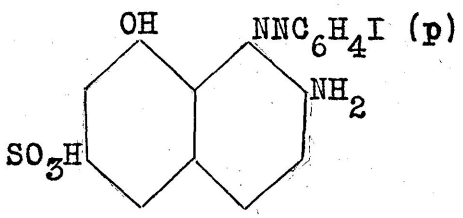
Theoretical percent of sodium	7.95	
Weight of sample	0.3000	0.3000
Weight of sodium sulphate	0.082	0.082
Percent of sodium found	8.84	8.84

The analysis for sodium was carried out as follows: The sample was weighed into a crucible and a small amount of sulphuric acid was added and the material ignited over a Bunsen burner. The ignition and addition of sulphuric acid was repeated until the dye had been entirely decomposed and only sodium sulphate remained. This was weighed and from the weight of sodium sulphate obtained, the percent of sodium in the dye was calculated.

Para iodo-aniline coupled with naphthalene 2-amino 8-hydroxy 6-sulphonic acid.

Equal molar part of the following were used; naphthalene 2-amino 8-hydroxy 6-sulphonic acid, para iodo-aniline and sodium nitrite. The para

iodo-aniline was dissolved in hydrochloric acid and the temperature reduced to 3 C. The sodium nitrite was dissolved in hydrochloric acid and its temperature reduced to 3 C. The sodium nitrite solution was slowly added to the iodo-aniline, with constant stirring. This results in the formation of p-iodo-benzene diazonium chloride. (See equation on Page 2) The naphthalene 2-amino 8-hydroxy 6-sulphonic acid was dissolved in strong sodium hydroxide solution and cooled to 3 C. To this solution the p-iodo-benzene diazonium chloride was slowly added with constant stirring. This results in the formation of a dye which probably has the following composition:

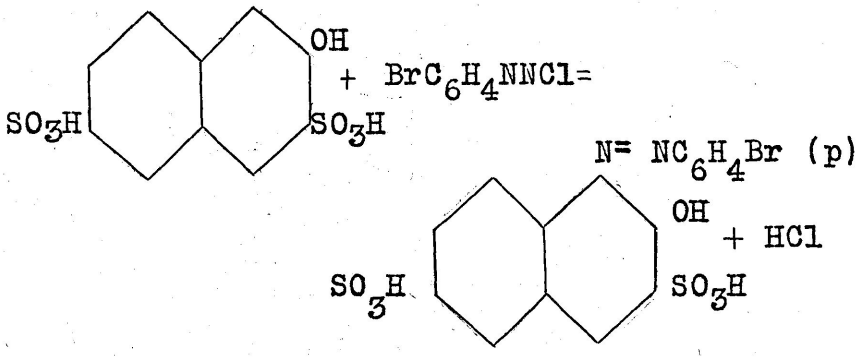


The dye was salted out and attempts were made to free it from sodium chloride, but this was unsuccessful. The dye and the salt would go into solution at the same rate, so no analyses for sodium were possible.

Para brom-aniline coupled with naphthalene 2-hydroxy 3-6-di-sulphonic acid.

Equal molar parts of the following were used; naphthalene 2-hydroxy 3-6-di-sulphonic acid, para brom-aniline and sodium nitrite. The para brom-aniline was diazotised in hydrochloric acid solution at 3 C. It was then coupled with naphthalene 2-hydroxy 3-6-di-sulphonic acid in sodium hydroxide solution, at 3 C.

(p) (p)
$BrC_6H_4NH_2$ -- HNO_2 = $2H_2O$ BrC_6H_4NNCl

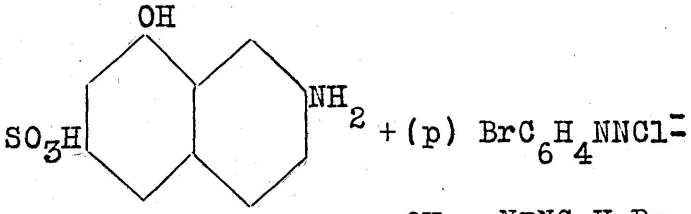


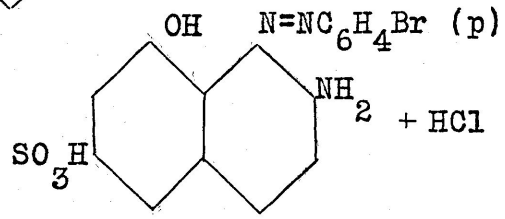
The dye, naphthalene 1- NNC H Br (p) 2- hydroxy 3-6-di-sodium sulphonate, was salted out and separated by filtration. It was washed to free it from salt. The analysis was as follows;

Theoretical percent of sodium	8.66	
Weight of sample	0.5000	0.5000
Weight of sodium sulphate	0.1610	0.1625
Percent sodium found	10.4	10.

Para brom-aniline coupled with naphthalene 2-amino 8-hydroxy 6-sulphonic acid.

Equal molar parts of the following were used; naphthalene 2-amino 8-hydroxy 6-sulphonic acid, para brom-aniline and sodium nitrite. The para brom-aniline was diazotised in hydrochloric acid solution at 3 degrees C., forming p-brom benzene diazonium chloride, which was then coupled with the naphthalene 2-amino 8-hydroxy 6-sulphonic acid in sodium hydroxide solution, at 3 C.



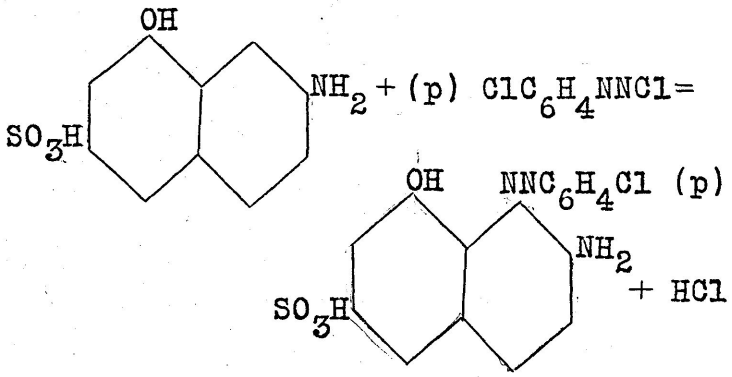


The dye was salted out and separated by filtration. It was washed to free it from salt. The analysis was as follows; which shows it to be naphthalene 1-NNC_6H_4Br (p) 2-amino 8-hydroxy 6-sodium sulphonate.

Theoretical percent of sodium	9.45	
Weight of sample	0.3000	0.3000
Weight of sodium sulphate	0.0880	0.0900
Percent of sodium found	9.49	9.71

Para-chlor-aniline coupled with naphthalene 2-amino 8-hydroxy 6-sulphonic acid.

Equal molar parts of the following were used; naphthalene 2-amino 6-8 di-sulphonic acid, para chlor-analine and sodium nitrite. The para chlor-aniline was diazotised in hydrochloric acid solution at 3 C., forming p-chlor benzene diazonium chloride, which was then coupled with the naphthalene 2-amino 6-8 di-sulphonic acid in sodium hydroxide solution, at 3 C.



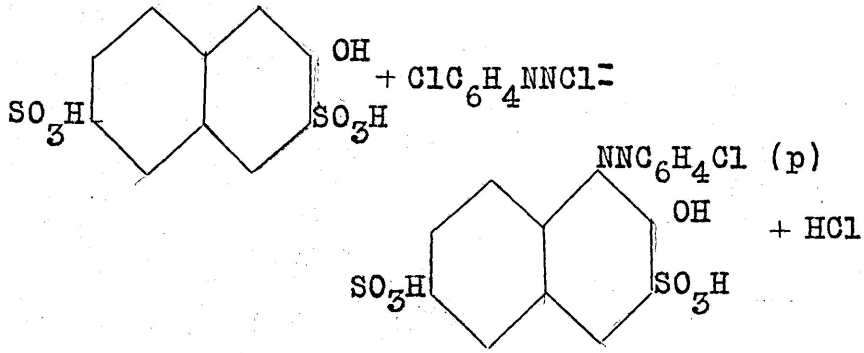
This dye, naphthalene 1 NNC_6H_4Cl (p) 2-amino 8-hydroxy 6-sodium sulphonate, was much less soluble than any of the preceeding dyes. No salting was required for its separation. It was filtered out, washed and dried.

Analysis.

Theoretical percent of sodium 5.77		
Weight of sample	0.300	0.300
Weight of sodium sulphate	0.0565	0.0560
Percent sodium found	6.09	5.71

Para chlor-aniline coupled with naphthalene 2-hydroxy 3-6-di-sulphonic acid.

Equal molar parts of the following were used; naphthalene 2-hydroxy 3-6-di-sulphonic acid, chlor-aniline and sodium nitrite. The para chlor-aniline was diazotised in hydrochloric acid solution at 3 C., forming p-chlor benzene diazonium chloride which was then coupled with the naphthalene 2-hydroxy 3-6- di-sulphonic acid in sodium hydroxide solution, at 3 C.

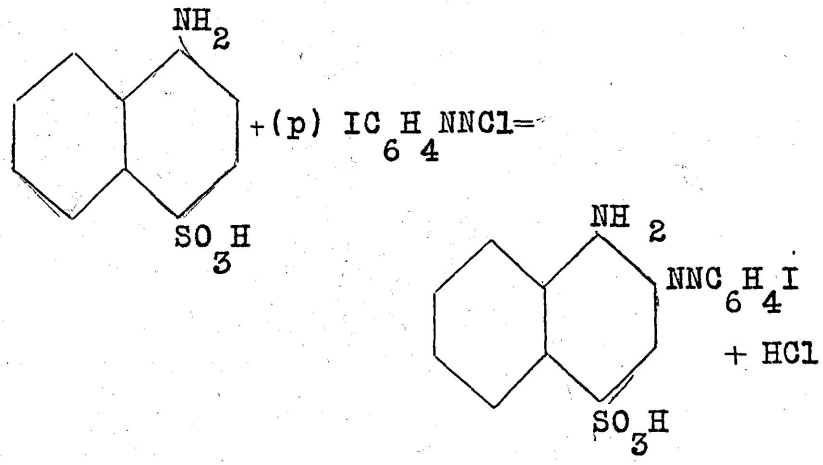


This dye, naphthalene 1-NNC_6H_4Cl (p) 2-hydroxy 3-6-di-sodium sulphonate, required no salting for its separation. Was filtered out, washed and dried. The analysis is as follows:

Theoretical percent of sodium	9.45	
Weight of sample	0.3000	0.3000
Weight of sodium sulphate	0.0880	0.0900
Percent sodium found	9.49	9.71

Para Iodo-aniline coupled with naphthionic acid.

Equal molar weights of the following were used; naphthionic acid, para iodo-aniline and sodium nitrite. The para iodo-aniline was diazotised in hydrochloric acid solution at 3 C., forming p-iodo benzene diazonium chloride, which was then coupled with naphthionic acid in sodium hydroxide solution, at 3 C.



The dye was salted out and separated by filtration. It was washed to free it from salt and dried. The analysis was as follows:

Theoretical percent of sodium	4.84	
Weight of sample	0.4220	0.4220
Weight of sodium sulphate	0.0600	0.0600
Percent sodium found	3.88	3.88

Bromination of para iodo-aniline.

The acet-anilid of para iodo-aniline was prepared and treated with bromine in a chloroform solution. One mole of the aniline to one-half mole of bromine were used. The iodine in the para position was not replaced by the bromine as was found by Malleis, no reaction took place. Next, one mole of para iodo-aniline was treated with one mole of bromine using no solvent. A reaction occurred giving off much heat. No heat was necessary to start a reaction. The reaction product was dissolved in alcohol from which it separated in light yellow needles, melting at 148-150 C. The iodine was retained and the bromine replaced the hydrogen in the (2) position of benzene ring, as shown by the following analyses. On treating the compound with MnO_2 and sulphuric acid iodine was evolved.

Theoretical % N in the 2-brom 4-iodo acetanilid	4.12
Theoretical % N in the 2-6-brom 4-iodo "	3.19
Theoretical % N in the 2-4-brom acetanilid	4.78

Analysis.

Sample	0.3000	0.3000
Standard HCl	20.50c.c.	20.00 c.c.
Standard NaOH	11.6 c.c.	11.4 c.c.

1 c.c. HCl= 0.0021 gm. nitrogen.
1 c.c. of alkali x 1.19= 1 c.c.acid.
Blank correction 0.19
Percent nitrogen found 4.53 4.38

These analyses give results for nitrogen between the theoretical for 2-brom-4-iodo acetanilid and 2-4-brom acetanilid, so analyses were made for the halogen content. Theoretical percent of I and Br in 2-brom 4-iodo acetanilid is ~~50.85~~ 60.09. Theoretical percent of Br in 2-4-brom acetanilid 54.57.

Analysis;

Sample	0.3000	0.3000 gm
Std. $AgNO_3$	45.7	49.0 c.c.
" KCNS	6.3	9.3 c.c.
KCNS factor	1.128	

6.3 c.c. KCNS=5.6 c.c.$AgNO_3$
9.3 c.c. " =8.2 c.c. "

$AgNO_3$ corrected	40.1 c.c.	40.8 c.c.

1 c.c. $AgNO_3$= 0.003465 gm Br.
" = 0.0055445 " I.

Assuming that half the $AgNO_3$ was used in combining with Br.and the other half with I,we have the following results: total halogen as I and Br= 61.11% and 61.26%. 60.79

Assuming that all the $AgNO_3$ was used in combining with Br. we have the following results.
Bromine= 46.66 and 46.73.
This shows the compound to be 2-Br 4-I acetanilid.

Pyrazolones.

Attempts were made to sulphonate the highly colored I-phenyl-3-methyl-4-para brom-anilido methylene-5keto pyrazolone and I-phenyl 3-methyl-4-benzal 5-keto pyrazolone using various strengths of concentrated sulphuric and fuming sulphuric acids. The results were the decomposition of the pyrazolones. None of the reaction products in the first case were identified. In the second case benzaldehyde was detected but the other products of the reaction were not identified.

Benzidin.

Attempts were made to substitute iodine in benzidin. The following were used:

Benzidin	9.8 gm.
Iodine	25.0 gm.
Calcium carbonate	12.0 gm.
Ether	30. c.c.
Water	20. c.c.

This mixture was heated on the water bath for 15 hours. The material was extracted and recrystalized. The melting point was taken, which

corresponded to that of benzidin. Moreover no iodine was detected by treating the compound with MnO_2 and sulphuric acid. Much free iodine was in the flask after heating. Apparently this method of preparing a substituted benzidin will not work.

Experiments in dyeing.

Fifteen grams of wool was soaked in water and then mordanted in a bath of the following composition:

Tartar emetic	1.2 gm.
Water	300. c.c.

After mordanting, the cloth was washed well to free it from excess mordant. It was now ready for dyeing. This was repeated using cotton and silk.

Fifteen grams of wool was soaked in water and then mordanted in a bath of the following composition:

Tannic acid	1.5 gm.
Water	300. c.c.

The mordanted cloth was washed well to free it from excess mordant. This was repeated using cotton and silk.

Dyeing.

All dyeing was carried out in a bath of the following composition:

Water	300. c.c.
Sodium sulphate	2.4 gm.
Sulphuric acid	1 c.c.

The weight of dye in bath is equal to 2% of the weight of the cloth to be dyed.

Method.

The dye (0.25 gm.) was weighed out and dissolved in 300 c.c. of water, 2.4 gm. of sodium sulphate was added. This was filtered to insure that no particles of undissolved dye would be in the bath. The filtered bath was then heated till luke warm. The proper amount of cloth (wet) was placed in the bath and the temperature slowly increased to the boiling point. It was allowed to simmer for about five minutes. Then 1 c.c. sulphuric acid was added and the heating continued until the cloth had absorbed practically all the dye in the bath. It was removed and washed thoroughly in several changes of water to free it from excess dye.

This method was carried out using cotton, wool and silk, both mordanted and unmordanted. The cotton was not effected at all when unmordanted and only very slightly effected when mordanted. The wool and silk were well colored in all cases.

In all cases the wool and silk were found to be fast to washing and sunlight. In the sunlight test, the samples were exposed for five weeks.

The darkest colors are produced by iodine and the lightest colors by chlorine. The iodine compounds are very soluble , but the chlorine compounds are so much less soluble, that salting is not necessary for their separation. In other words depth of color and solubility decrease with decrease in molar weight.

In conclusion, I wish to thank Dr. F.B.Dains, under whose direction this research has been conducted.

Naphthalene 1-NNC$_6$H$_4$I 2-hydroxy 3-6 di-sulphonic

Unmordanted | Tartar emetic mordant | Tannic acid mordant

Naphthalene 1-NNC$_6$H$_4$I 2-amino 8-hydroxy 6-sulphonic acid.

Unmordanted | Tartar emetic mordant | Tannic acid mordant

Naphthalene 2-NNC$_6$H$_4$I 1-amino 4-sulphonic acid.

Unmordanted | Tartar emetic mordant | Tannic acid mordant

Naphthalene 1-NN[illegible] Br 2-[illegible]roxy 3-6-sulphonic acid.

Unmordanted | Tartar emetic mordant | Tannic acid mordant

Naphthalene 1-NNC$_6$H$_4$Br [illegible]amino 8-hydroxy 6-sulphonic acid.

Unmordanted | Tartar emetic mordant | Tannic acid mordant

Naphthalene 1-NNC$_6$H$_4$Cl 2-hydroxy 3-6-di-sulphonic acid.

Unmordanted | Tartar emetic mordant | Tannic acid mordant

Naphthalene 1-NNC H Cl 2-amino 8-hydroxy 6- sulphonic acid.

Unmordanted | Tartar emetic mordant | Tannic acid mordant